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ScienceDirect

Energy Procedia 38 (2013) 753 – 759

Energy Procedia

SiliconPV: March 25-27, 2013, Hamelin, Germany

Influence of the chemicals used in nickel and copper plating solutions on the adhesion of screen-printed silver contacts

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Abstract

The present work deals with the attack of different chemicals used in nickel and copper plating electrolytes, on screen printed silver front side contacts, which lowers the adhesion and hinders industrial implementation. Dipping tests with four different self-made pastes in isolated electrolyte compounds show the dissolution of silver for pastes with glass content and acidic exposure conditions in chemical trace analysis (ICP-OES) of the dip solution. These results can be correlated to the macroscopic contact adhesion, measured with quantitative peel force tests. The results show that there is a link between the amount of silver that is found in the dipping solutions after the exposure of the contacts, the measured contact adhesion, and the presence of glass in the contact. The reaction between glass and silver during the firing process forms an oxidation layer between silver and glass which provides good adhesion. This interface seems to be dissolved by acidic plating chemicals. An additional SEM investigation shows the failure mechanism to take place exactly between the glass that covers the wafer after the firing process and the silver bulk, indicating a chemical attack at this interface.

Keywords: Seed & Plate, Electrolyte, Seedlayer, Silver Paste, Glass System, Adhesion, ICP/OES

1. Introduction and motivation

One way to substitute the expensive silver with cheaper copper for the front side metallization of silicon solar cells is to plate a stack of a nickel and copper on top of a printed fine line silver seed layer [1]. Copper provides the lateral conductivity, while nickel underneath acts as barrier layer to prevent copper from diffusing into the silicon wafer. This concept has the advantage that it could be realized by retrofitting existing production lines just with additional plating tools. A challenge with this metallization concept is the poor adhesion of the metal contact on the wafer after plating [2]. For module integration sufficient contact adhesion is crucial. Otherwise, the industrial soldering process based on tabber stringer

doi:10.1016/j.egypro.2013.07.343

systems for automatic soldering cannot be used. On this account it is important to get more information about the mechanism that lowers the adhesion during the nickel and the copper plating step in the process sequence.

2. Experiment

For the dipping experiments solar cell samples were produced by screen printing single busbars on standard wafers with silicon nitride anti reflection coating and a 75 Ω Emitter. The wafers did not have a backside metallization to eliminate the possibility of measuring dissolved elements from the backside paste in the chemical trace analysis. In order to know exactly what is in the front side contacts we used three different self-composed silver pastes with different glass systems to print the busbars. Table 1 shows the used front side silver pastes and their compounds.

Table 1. Used paste variations for the front side contacts

Paste	Contact forming system	Composition of the basic paste
Paste 1	3wt% lead glass	73wt% silver 24wt% binder and solvents
Paste 2	3wt% bismuth glass	
Paste 3	0.5wt% lead glass + 2.5wt% metal oxide	
Paste 4	basic paste without glass	

For comparability all the printed cells were fired in an inline belt furnace at the same set peak temperature of 900°C. I is possible that with an additional firing optimization, the adhesion results would have been improved depending on the paste, but this was not the subject of this work. However the general trends in the results between good and zero adhesion would not change dramatically.
The contacts were dipped for 10 minutes at room temperature in 15 ml of the listed chemicals in table 2. After the dipping the contacts were rinsed and dried before the soldering process.
Table 2 shows the used chemicals, the pH values and the related electrolytes in which the chemicals are usually used.

Table 2. Used chemicals for the dipping tests

Dipping solution	Molecular formula	pH-value	A substance of
Methane sulfuric acid (MSA)	CH_4O_3S	1	Rinse after Ag plating, tin electrolyte
Sulfuric acid	H_2SO_4	1	Copper electrolyte
Sulfuric acid	H_2SO_4	2.8	Copper electrolyte
Boric acid	H_3BO_3	3.8	Nickel electrolyte
Potassium hydroxide	KOH	12	Silver electrolyte

After the dipping experiment an evaluation of the dissolved elements in the dipping solutions by chemical trace analysis using an Agilent 700 tool for the ICP/OES measurement was done. The ICP/OES was calibrated with an ICP/OES standard solution before starting the measurement. In order to get into the calibrated field of the tool dilutions of the samples were prepared.

The busbars were manually soldered using a hotplate to pre heat the cells to a temperature of 65°C. The temperature of the soldering rod was 250°C. We used commercially available standard ribbons with a width of 1.5 mm and a standard flux.

The quantitative adhesion force measurement was done with an automated peel force tester (90° angle).

To evaluate the adhesion failure mode we did top view and cross section SEM-images and EDX-measurements of the contact area after peeling off the contacts.

3. Results

3.1 Correlation between the dissolved silver and the adhesion force

Figure 1 shows the silver content of the different dipping solutions (bar chart left axis) and additionally the average and maximal peel force values of the dipped busbars (red and blue curve right axis) after the busbar dipping experiments. The adhesion force values are normalized to the width of the soldered ribbon.

In case of methane sulfuric acid and sulfuric acid at pH 1 the adhesion values are null after 10 minutes exposure at the contacts for all pastes. This correlates well with the amount of silver that is the highest in these solutions after dipping. In the basic KOH solution and in the boric acid with a pH of 3.8 nearly no silver was found after dipping. The dissolution of silver out of the contact after dipping in the mentioned chemicals correlates with the pH. A lower pH leads to a higher silver amount measured in the dipping solution and also to a lower adhesion. Based on that, the use of electrolytes with a pH of 2.8 or higher is expected to help to improve adhesion after plating.

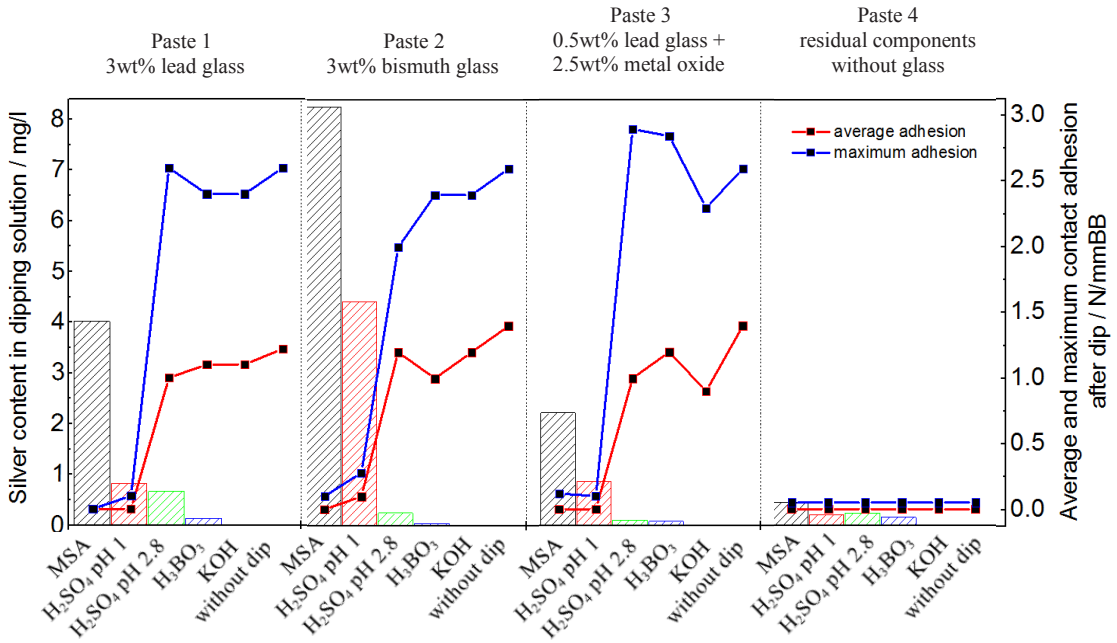


Fig. 1. Correlation between the amount of dissolved silver (left axis, bar chart) and the measured adhesion (right axis, average adhesion value red curve and maximum adhesion value blue curve). The x-axis shows the four different Ag-pastes.

The silver paste without glass (paste 4) did just form a very weak mechanical contact. The metallization sticks to the wafer after firing but the measured peel force was null for every sample. The amount of silver found in the solutions after dipping was significantly lower for paste 4 than for the other pastes, especially for dipping into methane sulfuric acid and sulfuric acid at pH 1. This means that the biggest part of the measured silver in the dipping solution is dissolved out of the glass and not out of the bulk silver of the contacts. Comparing paste 1 (3 wt% lead glass), paste 3 (0.5 wt% lead glass) and paste 4 (0 wt% lead glass) it can be seen that the measured silver concentration in the dipping solution is lower with a lower glass content in the paste. It can be concluded: If glass is present during the firing process a transition layer out of silver atoms and adjoining chemically bonded oxygen atoms, which are also part of the glass structure, is formed between glass and silver. This intermediate layer is responsible for providing good adhesion [3], and can apparently be dissolved by acidic solutions. The substitution of lead glass in the paste with bismuth glass did not show an advantage. The amount of dissolved silver with bismuth glass is the highest looking at methane sulfuric acid and sulfuric acid with pH 1. This shows that different glasses cause different silver dissolving rates. But it is highly questionable if a change in the glass system can solve the bad adhesion problem entirely because the oxidation layer between glass and is the one which is dissolved. To prevent this dissolution reaction a glass has to be developed which did not form this interface during the firing process. Additionally it is more complicated to change the glass system in a paste than to adapt the electrolyte with regards to pH.

3.2 SEM-images and EDX analysis of the contact area

The SEM image in Figure 2 shows a top view of the wafer surface after peeling off the soldered ribbon. As it can be seen the whole surface is covered with a remaining part of the glass layer with silver crystals underneath (position 2) except of some few spots were hole pyramids are ripped out (position 1).

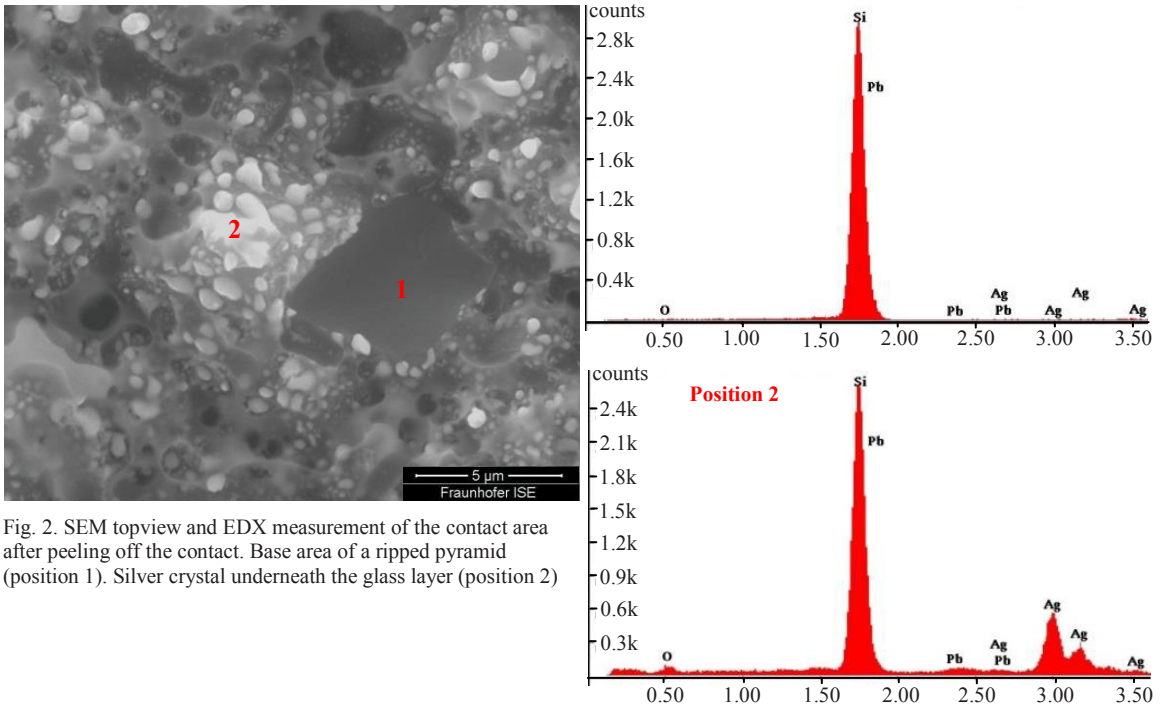


Fig. 2. SEM topview and EDX measurement of the contact area after peeling off the contact. Base area of a ripped pyramid (position 1). Silver crystal underneath the glass layer (position 2)

The surface looks very similar for every sample with an adhesion force of null. If the adhesion increases more ripped out pyramids are observed. For the samples with an adhesion average value >1N/mmBB the wafer breaks and there is no chance to see the interface. The EDX measurement proves that the white spots are silver crystals and the gray foursquare shaped area is the silicon base area of a ripped pyramid.

The SEM-images in figure 3 show a cross-section of the wafer surface after peeling off the soldered ribbon. It can be seen, that the silver crystals are located under the glass layer (a). The interface between silicon and glass is not affected. The bulk silver which was on top of the glass layer is entirely removed. The remaining glass layer is 200 nm to nearly 500 nm thick (b). It can be concluded that the failing interface is exactly between the glass layer and the bulk silver. The glass edges have a rounded shape this is another hint for an ongoing dissolution reaction where the glass is in contact with the bulk silver.

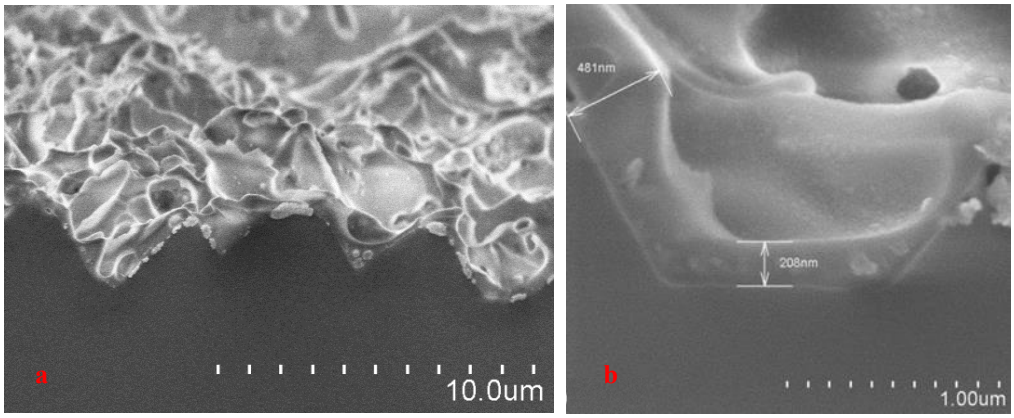
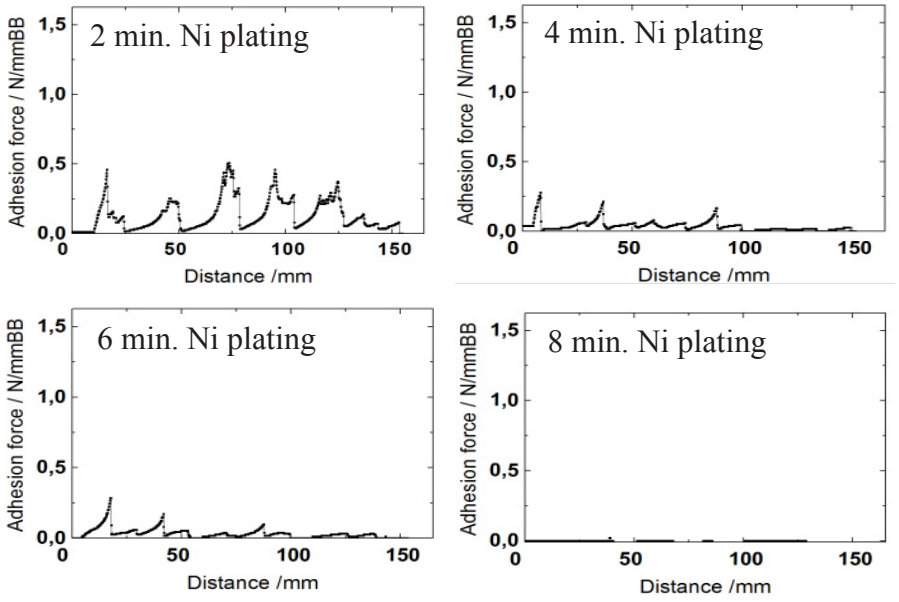


Fig. 3. SEM cross section of the contact area after peeling off the contact. Overview with crystallites that can be seen under the glass layer (a). Detail picture of the glass layer with thickness measurement (b).

3.3 Plating experiment

With the findings of the dipping tests a plating experiment was started to study the adhesion of low acidic electrolytes. We used nickel and copper electrolytes with pH >2. Busbars were plated with a nickel diffusion barrier a copper conducting layer and additionally a silver capping for solderability. For the plating we used an experimental lab setup. For the nickel plating a self-made Watts-type electrolyte with pH 2.5 including boric acid and nickel sulfate was used. For the copper plating, a commercially available electrolyte with a pH of 2.8 including sulfuric acid and copper sulfate was used. The busbars were soldered by putting 6 soldering spots on each busbar under reproducible conditions on an experimental soldering station were the soldering pressure and the temperatures of the soldering rod and the pre heat hot plate could be set very precisely. Figure 4 shows the adhesion-force diagrams of the plated busbars after the quantitative peel test. The plating times for nickel plating and the copper plating were varied. For the nickel plating, plating times between two and eight minutes were used in this experiment the copper plating time was constant at 10 minutes. For the copper plating, plating times between five and twenty minutes were used, in this experiment the nickel plating time was constant at 2 minutes. It can be seen very clearly that there is an adhesion drop due to increased nickel plating durations (fig 4 a). When the nickel plating time is constant and just the copper plating is increased the maximum peel force values get higher with higher copper plating times (fig 4 b). However the average peel force does not change much with increased copper plating times.

(a) nickel plating time variation with constant copper plating time of ten minutes



(b) copper plating time variation with constant nickel plating time of two minutes

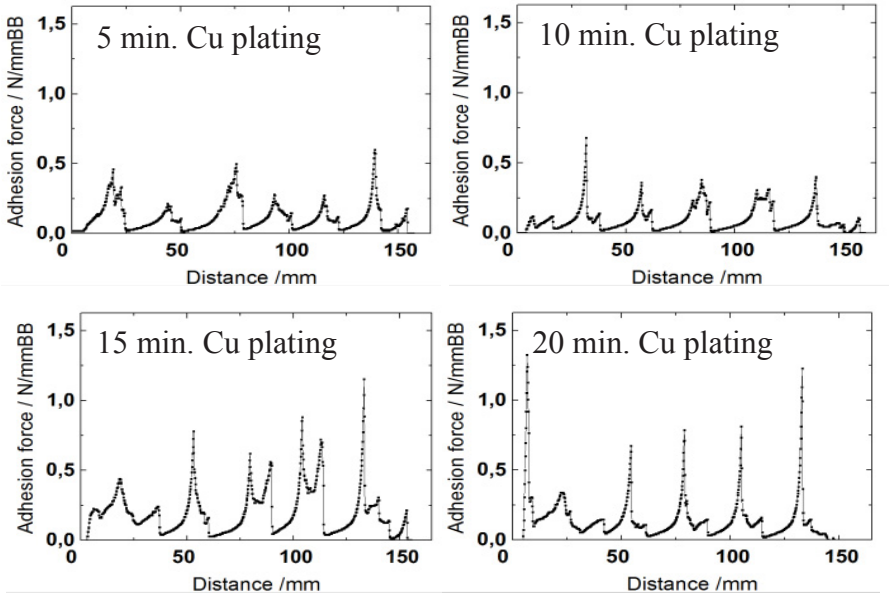


Fig. 4. Contact-adhesion-force measurement at varied nickel plating times (a) and copper plating times (b)

The adhesion drop is clearly caused by the nickel plating. Copper plating with a pH of 2.8 alone does not cause any adhesion problems. This result fits very well with the results of the former dipping tests where no negative influence of the sulfuric acid with a pH of 2.8 was observed. In the dipping tests the boric acid, which is the acidic component of the nickel electrolyte, does not lower the adhesion but the plating results show a clear adhesion drop. This means that there must be an additional effect that lowers the adhesion associated with the nickel electrolyte besides the direct pH correlation.

4. Conclusions

Dipping tests on solar cells with screen printed silver front side contacts, in isolated chemicals related to different plating electrolytes, show that the measured peel force correlates negatively with the amount of silver that is found in the solution after dipping. The highest amount of dissolved silver and the lowest measured peel force was observed in strong acidic solutions with a pH of 1. The alkaline solutions did not affect the measured peel force. If no glass was added to the paste nearly no silver was dissolved from the contact. The more glass is in the paste the more silver can be dissolved. This indicates that only silver that was oxidized by the glass frit is dissolved. It is known from literature that metal oxide provides the adhesion between metal and glass [3]. We conclude that an interface layer of oxidized silver between glass frit and bulk silver, which is responsible for the adhesion of the printed contacts can be dissolved by the chemicals and that this dissolution reaction cause low adhesion.

SEM and EDX analyses of the contact area after peeling off the contact show that the failing interface is exactly between the glass layer which covers the silicon after the firing process and the bulk silver. A substitution or reduction of the standard lead glass in the contact did not provide better stability against the used chemicals.

The plating experiment shows that in case of copper plating the adhesion problem could be solved using an electrolyte with a pH of 2.8. An interesting effect due to the nickel plating, which influences the contact peel-force in an adverse way, was observed. This effect could not be explained by the dipping experiment using boric acid out of the nickel electrolyte. We suggest that apart from hydronium ions there must be another ingredient or a combination of substances in the nickel electrolyte that accelerates the dissolution process and influences the contact peel force in a negative way. This behavior is currently under investigation in more detail in our group.

Acknowledgement

This work was partly supported by the German Federal Ministry of the Environment, Nature Conservation and Nuclear Safety (BMU) under the contract number 0325456 (KuLi).

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